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Abatement of Aqueous Anionic Contaminants by Thermo-responsive Nanocomposites: (Poly(N-isopropylacrylamide))-*co*- Silylanized Mg/Al Layered Double Hydroxides

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Abstract:

A series of novel thermo-responsive composite sorbents, were prepared by free-radical co-polymerization of N-isopropylacrylamide (NIPAm) and the silylanized Mg/Al layered double hydroxides (SiLDHs), named as PNIPAm-*co*-SiLDHs. For keeping the high affinity of Mg/Al layered double hydroxides towards anions, the layered structure of LDHs was assumed to be reserved in PNIPAm-*co*-SiLDHs by the silanization of the wet LDH plates as evidenced by the X-ray powder diffraction. The sorption capacity of PNIPAm-*co*-SiLDH (13.5 mg/g) for Orange-II from water was found to be seven times higher than that of PNIPAm (2.0 mg/g), and the sorption capacities of arsenate onto PNIPAm-*co*-SiLDH are also greater than that onto PNIPAm, for both As(III) and As(V). These sorption results suggest that reserved LDH structure played a significant role in enhancing the sorption capacities. NO_3^- intercalated LDHs composite showed the stronger sorption capacity for Orange-II than that of CO_3^{2-}. After sorption, the PNIPAm-*co*-SiLDH may be removed from water because of its gel-like nature, and may be easily regenerated contributing to the accelerated desorption of anionic contaminants from PNIPAm-*co*-SiLDHs by the unique phase-transfer feature through slightly heating (to 40^{o}C). These recyclable and regeneratable properties of thermo-responsive nanocomposites facilitate its potential application in the in-situ remediation of organic and inorganic anions from contaminated water.

Key words: PNIPAm; Layered double hydroxides (LDHs); Thermo-responsive; Sorption; Anionic contaminants; Regeneration

1. Introduction

Layered double hydroxides (LDHs), also referred to as hydrotalcite-like compounds, have received considerable attention in aqueous environment remediation due to their special layered structure and high affinities to anionic contaminants [1-3]. A generic formula for LDHs is: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}]_{x/n}\cdot zH_2O$, where M^{2+} and M^{3+} are divalent and trivalent cations consisting of the hydrotalcite-like layers; A^{n-} is a non-framework inorganic or organic anion for charge compensating [1]. LDHs can effectively remove the ionic chemicals, such as lead [4], radiocobalt [5], uranium (VI) [6], arsenate [7], as well as organic anions [8], dyes [9,10] by ion-exchange, chelation, adsorption, and so on. However, the application of LDHs in wastewater treatment is restricted by the difficulty of recycling of the LDHs from water [1]. For improving the recycle properties of LDHs, magnetic composites prepared by hybridizing magnetic cores such as Fe_3O_4 [11, 12], magnesium ferrite [13] and cobalt ferrite [14] were developed. These magnetic composites showed good recycling performance, whereas there are difficulties in thoroughly dispersion of granules in water. Therefore, the design of the unique composites based on LDHs that could be effectively recycled and easily regenerated is still crucial for the application of LDHs in waste water treatment.

LDHs have shown a good flexibility to hybrid with polymers and show the enhancement of mechanical or thermal stability properties to polymeric materials [12, 15, 16]. In these studies, the layered structures of LDHs are normally destroyed or exfoliated [17-21] and the naturally chemical and physical properties of LDHs crystals were ignored. However, keeping the layered structure of LDHs is worthwhile to the functional application of hybrid materials, since the physical and chemical properties

of LDHs can greatly impact on the sorption capability of LDH/polymer composites for the abatement of environmental contaminants. Therefore, how to protect the layered structure of LDH in the polymeric reaction is meaningful to improve the function of LDH/polymer composites.

Poly(N-isopropylacrylamide) (PNIPAm) **The equilibrium sorption capacities of Orange-II onto** thermo-responsive polymer [22-24] and it has been widely applied in drug control and release [25, 26], sensors [27], actuators [28], catalysts [29], smart hydrogels [30], smart hybrid hydrogel especially with clays[31-35], etc. PNIPAm can show a fast and sharp coil-globule phase transition with the change of the ambient temperature [36, 37]. We thus, supposed that covalently incorporation of PNIPAm into LDH could produce a new thermo-responsive nanocomposite. Placing this composite in water, it would spread out like a sponge and promote the sorption due to its dispersion into LDHs. And this composite could be easily removed from water because of its polymer-like nature. The thermo-responsive feature would be utilized to improve the desorption effciency of the LDH materials. Taking advantages of the temperature-induced aggregation and de-aggregation behavior like a sponge, the regeneration process for the LDH/polymer composites after sorption of the aqueous contaminants would be more easily and simply achieved.

In this study, a series of new thermo-responsive nanocomposites were prepared by a free-radical co-polymerization of NIPAm and the silylanized Mg/Al LDH with various mass ratios. The silanization process was induced by the hydrolysis of silane coupling agent (γ-Methacryloxypropyl trimethoxy silane, MPTS) on the surface of the wet LDH plates in order to protect the layered structure of LDH in co-polymerization

reaction. Two precursors, NO_3^- and CO_3^{2-} intercalated LDHs were used to reveal the influences of interlayer anions of LDH on the surface characteristics and the sorption properties of the nanocomposites. The microstructure of nanocomposites were characterized by X-ray powder diffraction, scanning electron microscope and Fourier transform infrared spectroscopy. *p*-(2-Hydroxy-1-naphthylazo) benzenesulfonic acid sodium salt (Orange-II) and arsenate anions (As(III) or As(V)) were selected as the target contaminants to investigate the sorption capacity of the nanocomposite. The regeneration experiment of the nanocomposite was conducted basing on its thermo-responsive properties. As expected, the prepared nanocomposites (PNIPAm-*co*-SiLDHs) with a gel-like feature can be easily picked out from the wastewater pools. And the used material can be regenerated by slightly heating to above 40^{o}C. This thermo-responsive material has the potential application in the in-situ remediation of anions polluted water.

2. Materials and Methods

2.1 Materials

The chemicals: $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, Na_2CO_3, $NaHCO_3$, NaOH, ethanol, 2,2'-Azo-bis-iso-butyronitrile (AIBN) and N,N'-Methylene bisacrylamide (MBA) were all purchased from Sinopharm Chemical Reagent Co., Ltd.,. γ-Methacryloxypropyl trimethoxy silane (MPTS, the silane coupling reagent) was purchased from NanJing Pinning Coupling Agent Co., Ltd. All chemicals were used as received. The N-isopropyl acrylamide (NIPAm) used for polymerization and *p*-(2-Hydroxy-1-naphthylazo) benzenesulfonic acid sodium salt (Orange-II) for sorption experiments were both purchased from TCI (Tokyo Chemical Industry Co.,

Ltd.). Arsenic standard solution was both purchased from O2si Company. To avoid CO_2 contamination, the double distilled solution was degassed by bubbling with nitrogen for 15 min, free of CO_2, to prepare the solutions in all the experiments.

2.2 Synthetic route of PNIPAm-co-SiLDH

The reaction schemes for the synthesis of SiLDHs and PNIPAm-*co*-SiLDHs are illustrated in scheme 1a and scheme 1b, respectively. Two different types of LDHs (CO_3-Mg/Al LDH and NO_3-Mg/Al LDH) were prepared by co-precipitation. As may be observed, the silane coupling agent γ-Methacryloxypropyl trimethoxy silane (MPTS) has two functional groups, alkoxysilane and acryl. To obtain the silanized LDH (SiLDH), the Si-OH groups which were formed after the hydrolysis of the alkoxysilane groups of MPTS, were condensed with M-OH (M: metal) groups on the surface of LDH by losing a portion of water.

2.2.1 Preparation of CO_3-Mg/Al LDH and NO_3-Mg/Al LDH

CO_3-Mg/Al LDH and NO_3-Mg/Al LDH were prepared in order to compare with the structures of MPTS modified LDH (SiLDH) and hybrid materials (PNIPAm-*co*-SiLDH). Compared to other ratios, CO_3-Mg/Al LDH and NO_3-Mg/Al LDH have a better adsorption capacity as reported, when the mole ratios of Mg/Al is 3:1 [38] and 2:1 [39], respectively. So the Mg/Al ratio of 3:1 for CO_3-Mg/Al LDH and 2:1 for NO_3-Mg/Al LDH has been chosen in the following experiments.

A hydrotalcite-type LDH with the Mg/Al ratio of 3:1 was prepared by co-precipitation, as described by Xu *et al* [7]. Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, 15.3 g, 60 mmol) and aluminium nitrate nonahydrate

139 ($Al(NO_3)_3 \cdot 9H_2O$, 7.5 g, 20 mmol) were dissolved in double distilled water before the
140 NaOH (6.4 g, 160 mmol) and Na_2CO_3 (4.25 g, 40 mmol) solution was added dropwise
141 and was stirred for 2 h at room temperature and aged at 65^oC for 24 h. Then filtered,
142 the excess salt in the residues was removed by washing them five times, after which
143 the residues of LDH (CO_3-Mg/Al LDH) were dried at 80^oC for 18 h and round to 100
144 mesh for further use.
145
146 To prepare NO_3-Mg/Al LDH (2:1), magnesium nitrate hexahydrate
147 ($Mg(NO_3)_2 \cdot 6H_2O$, 10.2 g, 40 mmol) and aluminium nitrate nonahydrate
148 ($Al(NO_3)_3 \cdot 9H_2O$, 7.5 g, 20 mmol) were dissolved in double distilled water before the
149 NaOH (4.8 g, 120 mmol) solution was added under the nitrogen atmosphere. The
150 suspension was stirred continuously for 2 h at room temperature and aged at 65^oC for
151 24 h. Then filtered, the excess salt in the residues was removed by washing them five
152 times, after which the residues of LDH (NO_3-Mg/Al LDH) were dried at 80^oC for 18
153 h and round to 100 mesh for further use.
154
155 *2.2.2 Synthesis of MPTS modified LDH (SiLDH)*
156 The MPTS is used to introduce ethylene groups onto the LDH surface. MPTS
157 modified CO_3-Mg/Al LDH and NO_3-Mg/Al LDH ($SiLDH_C$ and $SiLDH_N$) are
158 synthesized by tandem reaction synthesis method, as shown in Scheme 1a.
159 $Mg(NO_3)_2 \cdot 6H_2O$ (15.3 g) and $Al(NO_3)_3 \cdot 9H_2O$ (7.5 g) were dissolved in double
160 distilled water before the NaOH (6.4 g) and Na_2CO_3 (4.25 g) solution was added
161 dropwise and then was stirred for 2 h at room temperature and aged at 65^oC for 24 h.
162 After that, the supernatant was removed and MPTS (dissolved in ethanol) was added,
163 then suspension was stirred for 2 h under nitrogen atmosphere. For $SiLDH_N$,

$Mg(NO_3)_2 \cdot 6H_2O$ (10.2 g) and $Al(NO_3)_3 \cdot 9H_2O$ (7.5 g) was dissolved in double distilled water before the NaOH (4.8 g) solution was added dropwise under nitrogen atmosphere. The suspension was stirred continuously for 2 h at room temperature and aged at 65°C for 24 h. After that, the supernatant was removed and MPTS which was dissolved in ethanol was added, then suspension was stirred for 2 h under nitrogen atmosphere. Finally, the solid products ($SiLDH_C$ and $SiLDH_N$) were separated by filtration and washing, first with ethanol, then thoroughly with double distilled water. SiLDH were dried at 80°C for 18 h and then ground to 100 mesh. Thus, the ethylene groups were introduced onto the LDH surface and which can be used as the crosslinker in the polymerization of NIPAm.

2.2.3 Synthesis of PNIPAm-co-SiLDH

The polymerization experiments were conducted under nitrogen. 5 ml ethanol, NIPAm and SiLDH were charged into a 25 ml glass tube. During stirring at room temperature, the initiator (AIBN, 2 wt% of the monomer) was added. After that, the mixture was stirred at 60°C for a specified polymerization period. Finally, the formed gel-like products (PNIPAm-*co*-SiLDH) were separated and washed by ethanol and double distilled water, dried at 80°C for 18 h. In this study, the mass ratios of NIPAm and SiLDH are selected as 1:1, 3:1 and 5:1, the final products originated from $SiLDH_C$ are named as P/SC-1, P/SC-2 and P/SC-3, and that from $SiLDH_N$ were named as P/SN-1, P/SN-2 and P/SN-3, respectively.

2.2.4 Synthesis of PNIPAm

The PNIPAm is synthesized for the comparison with PNIPAm-*co*-SiLDH. The polymerization procedure of PNIPAm is conducted as follows: NIPAm monomer, crosslinking agent (N,N'-Methylene bisacrylamide, MBA) and ethanol were

dispersed in a 25 mL flask. The solution was stirred at 25°C under the stream of N_2 for 30 min. After that the initiator (2,2'-Azo-bis-iso-butyronitrile, AIBN) was added, and then the reaction temperature was raised to 60°C. After a specified polymerization period, the gel-like product (PNIPAm) was cooled and washed by ethanol and double distilled water for several times.

2.3 Characterization

Fourier transform infrared (FT-IR) spectroscopy was carried out using a Nicolet 380 FT-IR spectrometer (Thermo Fischer Scientific, Waltham, MA). Samples were analyzed as KBr discs with a 1% mass loading. The spectra were recorded between 4000 and 500 cm^{-1}.

X-ray powder diffraction (XRD) patterns were collected on a Rigaku D/MAX2200 X-ray diffractometer (Rigaku, Tokyo, Japan) instrument with Cu K_α radiation (λ = 0.15406 nm) in the 2θ range from 5° to 70° at the scanning speed of 8 °/min.

The metal concentrations in samples were determined by inductively coupled plasma-atom emission spectrometer (ICP-AES, Prodidy, Leeman Co) using dilute aqua regia as the dissolving agent. The content of total organic carbon (TOC, %) of the prepared samples were measured by the TOC analyzer (SSM-5000A, Shimadzu, Japan).

The surface structure images of materials were obtained by a SU-1500 (HITACHI, Japan) scanning electron microscope (SEM) after lyophilization. Energy-dispersive X-ray spectrometer (EDS) was attached to this instrument. All

specimens for SEM measurements are sputter-coated with gold for 40 s before observation.

The phase transition temperature of PNIPAm-*co*-SiLDH were characterized using differential scanning calorimetry (DSC) performed on a Perkin-Elmer Diamond DSC at a heating rate of 2 °C/min within 15-50 °C. Temperature accuracy of DSC is $\pm$ 0.1 °C.

The specific surface area of the samples was obtained by applying the BET-N_2 method using the Surface Area and Pore Size Analyzer NOVA2000E (Quantchrome Company, USA).

2.4 Sorption experiment

The sorption experiments of *p*-(2-Hydroxy-1-naphthylazo) benzenesulfonic acid sodium salt (Orange-II) onto PNIPAm-*co*-SiLDH and PNIPAm from water are conducted by mixing 0.01 g of dried solid sample with aqueous Orange-II solution in 25 mL glass tubes. The initial concentrations of Orange-II solution was 20 mg/L. The tubes were shaken at 90 rpm at room temperature for 5 h. After sorption, PNIPAm-*co*-SiLDH in the hydrogel form was easily picked out by a pair of tweezers from the solution. The supernatant concentration of Orange-II (λ_{max} = 484 nm) was determined by UV spectrophotometer (Unic UV-4802H) and the sorption products were also determined by XRD.

The sorption experiments of arsenate onto PNIPAm-*co*-SiLDH and PNIPAm from water were conducted by mixing 0.01 g of dried solid sample with arsenate solution (As(III) ~ 0.24 mg/L and As(V) ~ 0.85 mg/L) in 25 mL glass tubes. After the

mixture was oscillated for 12 h, the solid and liquid phases were separated by using 0.45 μm membrane filters. The concentration of As(III)/As(V) in supernatant was determined with atomic absorption spectrometry (AAS).

The sorption capacity, Q (mg contaminants per g sorbent), of sorbents was calculated using the following expression: Q (mg/g) = (C_0 - C_e) V/m, where C_0 and C_e are the initial and equilibrium concentrations of contaminants (mg/L), respectively, V is the volume of the solution added (L), and m is the amount of sorbent (g).

2.5 Regeneration experiment

After sorption of Orange-II, the gel-like solid was put into 10 mL 0.05M $NaHCO_3$ solution for regeneration. The mixture was first shaken at room temperature for 5 h and then heated for 0.5 h at 40 °C to remove the sorbed Orange-II, and the desorption amount was determined by the concentration of Orange-II in $NaHCO_3$ solution. Finally, PNIPAm-*co*-SiLDH was picked out and reused for the next run.

3. Results and Discussion

3.1 Characterization of PNIPAm-co-SiLDH

3.1.1 Evidence from FT-IR for the synthetic steps of PNIPAm-co-SiLDH

The Fourier transform infrared spectroscopy (FT-IR) spectra of samples formed at every step of the synthetic route (scheme 1a and scheme 1b) are shown in Figure 1. In Figure 1a and Figure 1b, the bridge band in ~ 3450 cm^{-1} is the stretching vibration of -OH groups for CO_3-Mg/Al LDH or NO_3-Mg/Al LDH. The band observed at ~ 1635 cm^{-1} is the bending vibration of the interlayer water. The strong and sharp band at ~ 1380 (~ 1384) cm^{-1} is attributed to the CO_3^{2-} (NO_3^-) located in interlayer space, and

the band at ~ 660 cm^{-1} is due to the M-O (M-O-H) stretching vibration (M = Mg^{2+}, Al^{3+}).

In order to obtain a silanized LDH (SiLDH), the Si-OH groups which are formed after the hydrolysis of the alkoxysilane groups of MPTS is reacted with -OH groups on the surface of LDH [40]. There are four main differences, which could confirm an effective silanization in FT-IR data. First, the new absorption bands at ~ 2917 and ~ 1719 cm^{-1} for SiLDH are representative of the stretching vibration of C-H (in $-CH_2$ and $-CH_3$) and the -COO- groups. Then, the much stronger and sharper bands at ~ 1635 cm^{-1} may be attributed to the C=C groups of MPTS. Meanwhile, the neoformative bands between 860 and 1200 cm^{-1} are assigned to stretching vibration of Si-O groups from silane, demonstrating the existence of siloxane in silanized samples (SiLDH) [40]. However, the intensity of the peak at 1050 - 1100 cm^{-1} which representative the Si-O-C groups becomes weaker. This implied that the major part of the methyl groups on MPTS have been substituted during the process of silylation. The multiple bands at ~ 670 cm^{-1} are assigned to stretching vibrations of M-O (M-O-H and M-O-Si) groups in SiLDH. All these changes evidence that MPTS has been successfully grafted onto the surface of LDHs.

The proposed free-radical co-polymerization process as shown in Scheme 1b was supported by FT-IR spectroscopic data. As shown in Figure 1, the typical double peaks at amide I band (~ 1650 cm^{-1}) and amide II band (~1554 cm^{-1}) can be observed in the spectra of P/SC-1, P/SC-2, P/SC-3, P/SN-1, P/SN-2 and P/SN-3. For PNIPAm-*co*-SiLDH, the band at about ~ 1635 cm^{-1} attributed to C=C stretching vibration of MPTS disappeared, due to the co-polymerization reaction. Moreover, the Si-O-M stretching vibration of the SiLDH (~ 670 cm^{-1}) can also be found in the

spectra of the hybrid materials. The results indicated that PNIPAm-*co*-SiLDH was constructed by the SiLDH sheets and polymerization of the NIPAm monomer. Due to the C=C bond on MPTS, the SiLDH might be the cross-linker on the network of PNIPAm-*co*-SiLDH. The peak for the carboxyl group at ~ 1719 cm^{-1} was no longer observed in the spectra of PNIPAm-*co*-SiLDH, possibly due to coverage of the surface with PNIPAm.

3.1.2 Evidence from X-ray diffraction for the Preserved layered structure of LDH

The Powder X-ray diffraction patterns of synthesized samples are presented in Figure 2a and 2b. Figure 2a shows the Powder X-ray diffraction patterns of CO_3-Mg/Al LDH, $SiLDH_C$, PNIPAm, P/SC-1, P/SC-2 and P/SC-3, respectively. Besides PNIPAm, all the samples exhibit the triple diffraction peaks and which are the unique feature of X-ray diffraction pattern of a hydrotalcite-like structure. CO_3-Mg/Al LDH had a diffraction band centered at d_{003} = 0.79 nm (2θ = 11.2°) [41]. Compared with CO_3-Mg/Al LDH, the interlayer spacing of $SiLDH_C$ was 0.78 nm and no reflection was detected at the lower 2θ angles, suggesting that the silylation reaction only occurred on the external surfaces of the LDHs. Meanwhile, PNIPAm-*co*-$SiLDH_C$, the interlayer spacing of the samples (P/SC-1, P/SC-2 and P/SC-3) was also about 0.79 nm. These results indicated that polymerization did not change the crystal structure of LDH and the layered structure of LDH was reserved. Compared with the pattern of PNIPAm, there is a similar large package between 15° to 30° in the patterns of SiLDH and PNIPAm-*co*-SiLDH, which may due to the amorphous of organic components.

In Figure 2b, the interlayer spacing of NO_3-Mg/Al LDH and $SiLDH_N$ were 0.90

316 nm and 0.88 nm, which are a little higher than that of CO_3-Mg/Al LDH and $SiLDH_C$
317 due to the different size of interlayer anions [21]. P/SN-1, P/SN-2 and P/SN-3 all have
318 the triple diffraction peak which suggested the layered structure of LDH. The
319 interlayer distance (d_{003}) of P/SN-1, P/SN-2 and P/SN-3 are around 0.88 nm (2θ about
320 9.8^o) and similar to NO_3-Mg/Al LDH and $SiLDH_N$, which demonstrated that the
321 layered structure belonged to NO_3-Mg/Al LDH is also preserved in
322 PNIPAm-*co*-$SiLDH_N$.
323
324 *3.1.3 Composition of PNIPAm-co-SiLDH*
325 The chemical compositions of the prepared materials are listed in Table 1. The
326 Mg/Al ratios of CO_3-Mg/Al LDH, $SiLDH_C$, P/SC-1, P/SC-2 and P/SC-3 is calculated
327 to be about 2.9:1, which is close to the expected ratio (3:1). Meanwhile, the Mg/Al
328 ratios of NO_3-Mg/Al LDH, $SiLDH_N$, P/SN-1, P/SN-2 and P/SN-3 is calculated to be
329 about 1.8:1, close to the expected ratio (2:1). The contents of organic carbon in
330 $SiLDH_C$, $SiLDH_N$, P/SC-1, P/SN-1, P/SC-2, P/SN-2, P/SC-3 and P/SN-3 are 9.34%,
331 9.99%, 25.93%, 30.49%, 39.24%, 41.62%, 40.82% and 45.42%, respectively. The
332 organic carbon contents of $SiLDH_C$ and $SiLDH_N$ are contributed to
333 γ-Methacryloxypropyl silane group which was induced by the slinanzation of LDH
334 with MPTS. The increasing trend of TOC values for P/SC-1, P/SC-2 and P/SC-3 as
335 well as P/SN-1, P/SN-2 and P/SN-3 indicated that the contents of organic components
336 inherited are raised with the enlargement of the mass ratio of NIPAm.
337
338 With the increasing content of LDHs in nanocomposites, the gel-like
339 nanocomposites PNIPAm-*co*-SiLDHs (in water) become more easily broken.
340 However, LDH component was supposed to the main sorptive zone in these
341 composites. Thus, P/SN-2 and P/SC-2, which had good gel-like performance in water

and the suitable content of LDHs, were selected as the typical sorbent and their micro-morphologies and sorption capacities for anionic contaminants were investigated.

3.1.4 Morphology of samples

The SEM images NO_3-Mg/Al LDH, $SiLDH_N$, P/SN-2 and P/SC-2 are shown in Figure 3. Comparing with the image of NO_3-Mg/Al LDH (Figure 3a), the $SiLDH_N$ (Figure 3b) seems to have a much smoother surface, as a result of the modification of MPTS. PNIPAm-*co*-SiLDH (P/SN-2 and P/SC-2) exhibits the porous structure with an average diameter about 8 μm. The large porous structure supplies a gallery for water to come in and out.

The EDS spectra of P/SN-2 are shown in Figure 3e. The rough part on the edge of the porous polymers (such as domain M) was the layers of LDH, which are proved by EDS. EDS spectrum showed the presence of Mg, Al and Si in domain M of P/SN-2, verifying the NIPAm crosslinked by $SiLDH_N$. The content of C and O in domain N is due to the organic part of PNIPAm. The EDS results demonstrated that the surface silanized LDH are dispersed in the PNIPAm and acted as multifunctional cross-linkers.

3.1.5 Thermoresponsive characteristics of PNIPAm-co-SiLDH

The thermoresponsive characteristics of PNIPAm and PNIPAm-*co*-SiLDH in water can be readily studied by Differential Scanning Calorimetry (DSC) curves to determine the coil-to-globule transition of these materials (Figure 4). As expected, both PNIPAm and PNIPAm-*co*-SiLDH samples have a LCST, which exhibit good thermoresponsive properties. Compared with PNIPAm with a LCST of 29.4 ^{o}C, the

LCST of P/SC-1, P/SC-2, P/SN-1, P/SN-2 and P/SN-3 is 27.5 ^{o}C, 28.9 ^{o}C, 28.6 ^{o}C, 28.3 ^{o}C, 28.3 ^{o}C, respectively. The LCST of the thermoresponsive polymers normally depends on the balance of hydrophobicity and hydrophilicity in the polymer structures. PNIPAm has the hydrophilic groups (acylamino) and the hydrophobic groups (isopropyl). Below the LCST of PNIPAm, the hydrogen bonding between amide groups and water molecules dissolute the polymer chains. And above the LCST, the hydrogen bonds are broken and water molecules are extruded from the polymer [22]. Therefore, the increasing content of the hydrophilic component makes the rise of the LCST, while the increasing content of the hydrophobic component makes the decline of the LCST. For PNIPAm-*co*-SiLDHs, the introduction of SiLDHs which are covered with silane propenyl groups on its external surface increases the hydrophobicity of this hybrid material and results in the decreased of the LCST.

3.2 Sorption and desorption ability of PNIPAm-co-SiLDH for Orange-II

The pollutions of organic and inorganic contaminants in water have gained so much attention due to their high toxicity. *p*-(2-Hydroxy-1-naphthylazo) benzenesulfonic acid sodium salt (Orange-II) and arsenate solution were selected as the target contaminants to investigate the sorption capacity of PNIPAm-*co*-SiLDH.

The sorption (Q_s) and desorption (Q_d) amounts of Orange-II with the initial concentration of 20 mg/L by P/SN-2, P/SC-2 and PNIPAm are shown in Table 2. The equilibrium sorption capacities of Orange-II (Q_s) onto P/SN-2, P/SC-2 and PNIPAm are 13.5, 5.7 and 2.0 mg/g. The weak sorption of Orange-II onto PNIPAm might attributed to the hydrophilic surface of PNIPAm which generated by the the hydrogen-bonding formed between water and the amino groups on surface of

PNIPAm. For 20 mg/L Orange-II solution, the equilibrium sorption capacities by CO_3-Mg/Al LDH and NO_3-Mg/Al LDH are 36.0, and 37.9 mg/g (see SI, Table S1). Much greater sorption capability of LDH than PNIPAm suggested the significant role of LDHs component in the sorption process for P/SN-2 and P/SC-2.

Based on the respective content of two components (LDH and PNIPAm) in P/SN-2, P/SC-2 (see Table 1) as well as their sorption capacities of pure LDH and PNIPAm, the expected sorption amounts of nanocomposites (11.5 mg/g for P/SN-2 and 10.4 mg/g for P/SC-2) are also calculated as shown in Table S1(SI). The greater experimental sorption capacities of P/SN-2 than the expected values demonstrated that the synergistic effect of LDH and PNIPAm for the uptake of Orange-II by PNIPAm-*co*-SiLDH$_N$. However, the experimental sorption capacity of P/SC-2 was even lower than the expected values. The difference of sorption capacities between P/SN-2 and P/SC-2 could be explained by their different microstructure and surface areas.

The specific surface areas of PNIPAm, P/SC-2 and P/SN-2 are determined to be 68, 28 and 86 m^2/g, respectively, as listed in Table 2. Due to the hydrophilic surface formed by hydrogen-bonding, PNIPAm shows very weak sorption to Orange-II, though it has a relatively large surface area (68 m^2/g). So we calculated the number of stacked LDH sheets (n) according to the Scherrer Formula ($D = 0.89\,\lambda / \beta(\theta)\cos\theta$) [42] and X-ray diffraction data (d_{003} values) (see in Table S2). The calculated sheets stacking number of P/SN-2 (n =11.7) is much lower than that of P/SC-2 (n =18.1), which implies the LDH crystal size on P/SN-2 is smaller than on P/SC-2 [42, 43]. The smaller crystal size made much larger external surface area of LDH exposed on P/SN-2 than on P/SC-2. These calculated results are consistent with the detected surface area of P/SN-2 (86 m^2/g) than P/SC-2 (28 m^2/g).

418 The XRD patterns of sorption products are shown in Figure S1. For
419 PNIPAm-*co*-SiLDH$_C$ and PNIPAm-*co*-SiLDH$_N$, the interlayer spacing did not change
420 much after sorption, it could be speculated that the sorption mainly occurred on the
421 external surface of LDHs. All these results indicated that NO_3^- would be more suitable
422 interlayer anion of LDH than CO_3^{2-} for nanocomposites PNIPAm-*co*-SiLDH.
423
424 After sorption, the synthesized thermoresponsive was easy to be regenerated.
425 The portion of solutes on sorption products can be easily removed by slightly heated
426 at 40 °C in $NaHCO_3$ solution. The coil-globule phase transition by heating greatly
427 accelerated the desorption process (within 0.5 h). The results of recycling experiment
428 are shown in Table 2. After the first cycle, the desorption amount is about 4.9 mg/g,
429 with a loss (~ 60%) in sorption capacity for P/SN-2. For the next four cycles, the dye
430 removal efficiency maintained at 90%. The convenient recyclable properties of
431 PNIPAm-*co*-SiLDH facilitate its potential application in the in-situ remediation of
432 anion contaminated water.
433
434 *3.3 Sorption ability of PNIPAm-co-SiLDH for arsenate*
435 The sorption results of the mixed arsenate (the initial concentration of As(III) and
436 As(V) was 0.24 and 0.85 mg/L, respectively) onto PNIPAm-*co*-SiLDH$_N$ and PNIPAm
437 from water are shown in Table 3. The equilibrium sorption capacities of arsenate onto
438 SLDH$_N$, P/SN-2 and PNIPAm are 0.17, 0.14 and 0.06 mg/g for As(III), and 1.69, 0.46
439 and 0.10 mg/g for As(V). Under pH = 7, As(III) is in a molecular form (H_3AsO_3) as
440 well as As(V) is in the form of $HAsO_4^{2-}$/$H_2AsO_4^-$ [44]. So the affinity of positively
441 charged LDH surface to As(V) would be stronger than that to As(III). Both for As(III)
442 or As(V), sorption capacities of arsenate onto PNIPAm-*co*-SiLDH were also greater

than that onto PNIPAm. Since the gel-like form of PNIPAm-*co*-SiLDH could be conveniently transferred after sorption, this nanocomposite could be applied as a unique sorbent in the in-situ remediation for As (III) or As (V) polluted water.

4. Conclusions

The novel thermoresponsive nanocomposites PNIPAm-*co*-SiLDHs were prepared from NIPAm monomer and the silanized layered double hydroxides (SiLDH) by free-radical polymerization. The sorption capacities of P/SN-2 for Orange-II, As(III) and As(V) from water were all greater than that of PNIPAm. NO_3^- intercalated LDHs composite showed the stronger sorption capability for Orange-II than that of CO_3^{2-} which due to the larger exposed external surface of the NO_3^- intercalated LDH nanocomposite. After sorption, the PNIPAm-*co*-SiLDH could be flexibly transferred from water in the gel-like form, and easily regenerated contributing to the accelerated desorption process by the unique phase transition through slightly heating. These recyclable and regenerable properties of thermoresponsive nanocomposite facilitate its potential application in the in-situ remediation of organic and inorganic anions contaminated water.

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